Calculation of Nuclear Magnetic Shielding Constants in Two Simple Systems

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determines the diffraction envelope using $F=2.5$ eV/Å for the external field). The analogous interference effects for the case of the field-emission potential occur only for energies above the top of the potential barrier[7–11] due to the narrowness of the potential hole between the image potential and the metallic surface. Therefore, as field emission occurs for electrons at the Fermi energy, far below the top of the barrier, the interference effects do not occur. They are visible only as periodic deviations from the Shottky line in the thermionic emission of electrons whose energy is near the top of the field-emission potential barrier.[7–11] Similarly, in the calculations using Models III and IV the additional interference effects due to the shape of the surface are not visible on the energy scale shown in the figures if the surface thickness is less than 0.01 Å.

The failure of the interference oscillations obtained using Models I, II, and III to damp out with the increasing width of the surface is due to the nonanalytic character of the potentials at the various joining points. The use of Model IV which transfers the discontinuity in the potential from the first to the second derivative does not mitigate this result. The effects of nonanalytic joining points in the potential on the transmission coefficient have been emphasized by Cutler and Davis[11] who find that similar results occur in field and thermionic emission due to the artificial joining of the image potential to the constant potential inside the metal. In general, the WKBJ approximation is valid only when these interference effects can be neglected. Therefore, it never predicts such effects, whereas artificially joined potentials predict interference patterns which decay too slowly with increasing E_d. For an (physically correct) analytic potential, the interference oscillations damp out above energies at which the rate of change of the electrons' wavelength in the regions of rapidly varying potential is small relative to the wavelength itself.[17] These remarks indicate that simple nonanalytic potentials, which we and others[5,10,11] have employed, overestimate the interference effects and are useful only as qualitative indicators of the nature of the effects. Furthermore, experiments in which these effects are detected probe sensitive details of the surface of the metal, hence experimenters should carefully verify their reproducibility.

ACKNOWLEDGMENT

The authors are indebted to Dr. Gert Ehrlich for suggesting this problem to them, and for helpful and critical discussions concerning it.

[17] See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), pp. 184–188.

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Calculation of Nuclear Magnetic Shielding Constants in Two Simple Systems

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The nuclear magnetic shielding constants of two simple systems are calculated explicitly. These systems are (1) a nucleus μ at a distance R from a hydrogenic atom of charge ζe in the presence of an external electric field, and (2) a nucleus μ of a hydrogenic atom of charge ζe in the presence of a point charge at R with the result expanded in inverse powers of R. These calculations should prove useful in understanding the long-range contributions of functional groups and neighboring molecules to observed chemical shifts of molecules.

I. INTRODUCTION

IN this paper we consider two model systems simple enough to allow rather complete solutions for their nuclear magnetic shielding constants. The results of both calculations can be useful in our understanding of real physical systems. First we obtain the magnetic shielding due to a hydrogen atom in a uniform electric field, $\mathcal{E}$, for a nucleus located at a large distance R from the hydrogen nucleus in the direction of the electric field. The linear effect of the electric field on the chemical shielding constant is given in closed form as a function of R and contains only exponentially decreasing terms.[1]

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[1] H. F. Hameka, Nuovo Cimento **11**, 395 (1959).

We next obtain the chemical shift of a hydrogenic atom of nuclear charge ζe perturbed by a positive charge Ze. The chemical shielding constant is expressed in a series in inverse powers of R, the distance between the nucleus and the perturbing positive charge and terms up to those in R^{-8} are included. For reasonable distances ($R\sim 5$ a.u.) the term in R^{-4} is about 70% of the total. Therefore the terms in R^{-6}, R^{-7}, and R^{-8} are not entirely negligible. This model can help us understand the effect of nonuniform fields on shielding constants.

II. MODEL (1)

A. Theory

For the first model consider a hydrogenic atom of nuclear charge ζe (possessing no nuclear moment) in a uniform electric field $\mathcal{E}$ in the z direction and in a uniform magnetic field $\mathbf{H}$. We want to compute the magnetic shielding due to this hydrogenic atom for a nuclear moment $\boldsymbol{\mu}$ at a point R on the z axis. The z axis points from the hydrogenic nucleus (Position a) to the nuclear moment (Position b). In the absence of the nuclear moment $\boldsymbol{\mu}$ and the fields $\mathcal{E}$ and $\mathbf{H}$, the Hamiltonian is simply

$$\mathcal{H}_0=(p^2/2m)-\zeta(e^2/r_a). \tag{1}$$

The conjugate momentum of $\mathbf{r}$ for a single particle of change $-e$ in the presence of a vector potential $\mathbf{A}$ is $[\mathbf{p}-(e/c)\mathbf{A}]$ and thus the difference between the total Hamiltonian in the presence of $\boldsymbol{\mu}$, $\mathcal{E}$, and $\mathbf{H}$ and $\mathcal{H}_0$ is (excluding the nuclear Zeeman term, $-\boldsymbol{\mu}\cdot\mathbf{H}$)

$$-(e/2mc)(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})+(e^2/2mc^2)A^2-e\mathcal{E}\cdot\mathbf{r}. \tag{2}$$

$\mathbf{A}$ is the magnetic vector potential which is composed of two terms, $\mathbf{A}_H$ and $\mathbf{A}_\mu$. $\mathbf{A}_H$ is the vector potential due to a constant magnetic field $\mathbf{H}$ and $\mathbf{A}_\mu$ the potential associated with the field due to the nuclear moment $\boldsymbol{\mu}$ at Position b

$$\mathbf{A}_H=\tfrac{1}{2}\mathbf{H}\times(\mathbf{r}_b-\mathbf{R}), \tag{3}$$

$$\mathbf{A}_\mu=(\boldsymbol{\mu}\times\mathbf{r}_b)/r_b^3, \tag{4}$$

where we have chosen $\mathbf{A}_H$ in a convenient coordinate system for our calculations.

We now write the Hamiltonian, Eq. (2), as a sum of four perturbations

$$\mathcal{H}_{1000}=-(e\hbar/2mci)\mathbf{H}\cdot\mathbf{r}_a\times\nabla, \tag{5a}$$

$$\mathcal{H}_{0100}=-(e\hbar/mci)(\boldsymbol{\mu}\cdot\mathbf{r}_b/r_b^3)\times\nabla, \tag{5b}$$

$$\mathcal{H}_{0010}=(e^2/2mc^2)(\mathbf{H}\times\mathbf{r}_a)[(\boldsymbol{\mu}\times\mathbf{r}_b)/r_b^3], \tag{5c}$$

$$\mathcal{H}_{0001}=-e\mathcal{E}\cdot\mathbf{r}_a, \tag{5d}$$

neglecting terms quadratic in $\boldsymbol{\mu}$ or $\mathbf{H}$ which are not related to the chemical shielding constant. The total Hamiltonian $\mathcal{H}$ is now

$$\mathcal{H}=\mathcal{H}_0+\lambda\mathcal{H}_{1000}+\mu\mathcal{H}_{0100}+\nu\mathcal{H}_{0010}+\omega\mathcal{H}_{0001}. \tag{6}$$

We have introduced four parameters λ, μ, ν, ω and expand the eigenfunction and eigenvalue of the total Hamiltonian, Eq. (6), in a power series in these parameters rather than in μ, H, and $\mathcal{E}$. The essential role of the parameters, which are assigned the value of unity, is to define the different orders of perturbation. The eigenvalue E and eigenfunction Ψ can be expanded as

$$E=\sum_{l,m=0}^{\infty}\sum_{p,q=0}^{\infty}\lambda^l\mu^m\nu^p\omega^q E_{lmpq}, \tag{7}$$

$$\Psi=\sum_{l,m=0}^{\infty}\sum_{p,q=0}^{\infty}\lambda^l\mu^m\nu^p\omega^q\Psi_{lmpq}. \tag{8}$$

The change in the shielding constant $\Delta\sigma$ linear in the electric field is obtained from the terms in the energy, Eq. (7), trilinear in μ, H, and $\mathcal{E}$. Thus

$$\boldsymbol{\mu}\cdot\Delta\sigma\cdot\mathbf{H}=E_{0011}+E_{1101}. \tag{9}$$

These energies are obtained using coupled perturbation theory by substituting Expressions (6), (7), and (8) into the Schrödinger equation

$$(H-E)\Psi=0 \tag{10}$$

and equating the coefficients of every power of $(\lambda\mu\nu\omega)$ to zero. After some manipulation E_{0011} and E_{1101} are found to be

$$E_{0011}=2\langle 0\mid\mathcal{H}_{0010}\mid 0001\rangle \tag{11}$$

and

$$E_{1101}=2\langle 0\mid\mathcal{H}_{0100}\mid 1001\rangle \tag{12}$$

when written in their most convenient form. The change in notation from Eq. (8) should be obvious, e.g., $\mid 1001\rangle=\psi_{1001}$. The evaluation of these energies requires the solutions to two partial differential equations

$$(\mathcal{H}_0-E_0)\mid 0001\rangle=-\mathcal{H}_{0001}\mid 0\rangle \tag{13}$$

and

$$(\mathcal{H}_0-E_0)\mid 1001\rangle=-\mathcal{H}_{1000}\mid 0001\rangle-\mathcal{H}_{0001}\mid 1000\rangle. \tag{14}$$

The first of these equations possesses the well-known solution of the hydrogen atom perturbed by an electric field and the second possesses a solution given in closed form below which describes the hydrogen atom perturbed by both an electric and magnetic field. There are other expressions for these energies such as

$$E_{1101}=2\langle 0\mid\mathcal{H}_{0001}\mid 1100\rangle, \tag{15}$$

but all of these involve solutions to partial differential equations which are difficult if not impossible to obtain in closed form.

B. Calculation and Results

One is usually interested in the trace of the shielding tensor and thus we evaluate

$$\langle\Delta\sigma\rangle_{Av}=\tfrac{1}{3}\mathrm{Tr}(\Delta\sigma_1+\Delta\sigma_2), \tag{16}$$

where $\Delta\sigma_1$ and $\Delta\sigma_2$ arise from E_{0011} and E_{1101}, respectively. If the constant electric field is perpendicular to R, $\langle\Delta\sigma\rangle_{Av}$ vanishes, there only being a change in σ quadratic in $\mathcal{E}$ for reasons of symmetry. When $\mathcal{E}$ is parallel to R, $\langle\Delta\sigma\rangle_{Av}$ is nonvanishing. The functions we need are

$$\psi_0=(1/\sqrt{\pi})\,(\zeta/a_0)^{3/2}\exp(-\zeta r_a/a_0), \tag{17}$$

$$\psi_{0001}=(2\sqrt{\pi})^{-1}\left(\frac{\zeta}{a_0}\right)^{3/2}\frac{1}{\zeta^3}\frac{a_0^2}{e}\,\mathcal{E}_z \times\left(\frac{\zeta^2}{a_0^2}r_a^2+2\frac{\zeta}{a_0}r_a\right)\exp(-\zeta r_a/a_0)\,\mathrm{P}_1(\cos\theta_a), \tag{18}$$

$$\psi_{1001}=-\frac{1}{12\zeta^2}\left(2\frac{\zeta^3}{a_0^3}r_a^3+11\frac{\zeta^2}{a_0^2}r_a^2+22\frac{\zeta}{a_0}r_a\right) \times\exp\left(-\zeta\frac{r_a}{a_0}\right)(\Delta_1\sin\theta\sin\phi+\Delta_2\sin\theta\cos\phi), \tag{19}$$

where

$$\Delta_1/12\zeta^2=(ia_0^4/24\sqrt{\pi}\zeta^5\hbar c)\,(\zeta/a_0)^{3/2}\,\mathcal{E}_zH_x. \tag{20}$$

The coefficient Δ_2 is defined similarly except H_x is replaced by H_y. From Eqs. (5c), (11), (16), and (18),

$$\tfrac{1}{3}\mathrm{Tr}\Delta\sigma_1=(2e^2/3mc^2)\,\langle 0001\mid(1/r_b)+(Rz_b/r_b^3\mid 0\rangle. \tag{21}$$

The integrals are simple. We get

$$\tfrac{1}{3}\mathrm{Tr}\Delta\sigma_1=(e^2/3mc^2a_0)\,(a_0^2/e)\,(\mathcal{E}_z/\zeta^2) \left[-\tfrac{9}{2}\rho^{-2}+\rho^{-2}(\tfrac{9}{2}+9\rho+9\rho^2+8\rho^3+7\rho^4+2\rho^5)\exp(-2\rho)\right], \tag{22}$$

where $\rho=\zeta R/a_0$. Also

$$\tfrac{1}{3}\mathrm{Tr}\Delta\sigma_2=\frac{e^2}{3mc^2a_0}\frac{1}{6}\frac{a_0^2}{e}\,\mathcal{E}_z\frac{\rho}{\zeta^2} \times\left\langle f\left(\zeta\frac{r_a}{a_0}\right)\frac{\exp(-\zeta r_a/a_0)}{r_b^3}\sin^2\theta_a\right\rangle, \tag{23}$$

where $f[\zeta(r_a/a_0)]$ is the radial part of Eq. (19) and the ϕ integration has been carried out. Evaluation of Eq. (23) leads to

$$\tfrac{1}{3}\mathrm{Tr}(\Delta\sigma_2)=(e^2/3mc^2a_0)\,(a_0^2/e)\,\mathcal{E}_z(1/\zeta^2) \times\left[\tfrac{9}{2}\rho^{-2}-\rho^{-2}(\tfrac{1}{3}\rho^4+\tfrac{17}{6}\rho^3+9\rho^2+9\rho+\tfrac{9}{2})\exp(-2\rho)\right]. \tag{24}$$

Adding Eq. (24) to Eq. (23) one obtains

$$\langle\Delta\sigma\rangle_{Av}=(e^2/3mc^2a_0)\,(a_0^2/e)\,\tfrac{1}{6}\mathcal{E}_z \times(12\rho^3+40\rho^2+31\rho)\exp(-2\rho). \tag{25}$$

TABLE I. $\langle\Delta\sigma_1\rangle_{Av}$, $\langle\Delta\sigma_2\rangle_{Av}$, and $\langle\Delta\sigma\rangle_{Av}$ [Eqs. (22), (24), and (25)] as functions of R for $\zeta=1.2$.

R (a.u.)	$\langle\Delta\sigma_1\rangle_{Av}\times10^{12}$	$\langle\Delta\sigma_2\rangle_{Av}\times10^{12}$	$\langle\Delta\sigma\rangle_{Av}\times10^{12}$
1.4	0.318	0.605	0.923
1.8	0.112	0.485	0.597
2.2	−0.026	0.380	0.355
2.6	−0.100	0.298	0.199
3.0	−0.129	0.235	0.106
3.4	−0.133	0.188	0.055
3.8	−0.125	0.153	0.028
4.2	−0.113	0.126	0.014

The change in σ, Eq. (25), contains only exponentially decreasing terms. The two parts of $\langle\Delta\sigma\rangle_{Av}$, i.e., $\frac{1}{3}\mathrm{Tr}\Delta\sigma_1$ and $\frac{1}{3}\mathrm{Tr}\Delta\sigma_2$, separately contain a R^{-2} dependence but these exactly cancel out. The terms $\Delta\sigma$ and $\Delta\sigma_2$ are sometimes, but nonuniquely, referred to as the "diamagnetic" and "paramagnetic" parts of the shielding constant. The over-all $\langle\Delta\sigma\rangle_{Av}$ is always positive, indicating that if electrons are drawn by the field towards the point R, the location of the nuclear moment, the result is an increased chemical shift. If the calculation is done for a point, $-R$, i.e., to the left of the hydrogenic atom, we will have a decreased chemical shift.

In Table I we give values of $\langle\Delta\sigma_1\rangle_{Av}$, $\langle\Delta\sigma_2\rangle_{Av}$, and $\langle\Delta\sigma\rangle_{Av}$ [Eqs. (22), (24), and (25)] for $\zeta=1.2$ and R ranging from 1.4 to 4.0 a.u. We select $\zeta=1.2$ as this is the effective nuclear charge usually assigned to an H atom in a molecular calculation. Note that $\langle\Delta\sigma_1\rangle_{Av}$ can be negative or positive. Although the value of $\langle\Delta\sigma\rangle_{Av}$ for $\zeta=1.2$ and $R\sim1.4$ a.u. is $\sim10^{-12}$ one cannot seriously relate this value to those found in actual molecular calculations, e.g., the linear electric field effect on σ of the H_2 molecule.

Hameka[1] calculated the long-range chemical shift due to a hydrogen atom in a uniform electric field but expanded $\Delta\sigma$ in inverse powers of R. Thus

$$\Delta\sigma=[-(e^2/2mc^2)\,\langle 0\mid\mathbf{\hat{1}}\mathbf{r}_0\cdot\hat{\imath}-\mathbf{r}_0\hat{\imath}\mid 0\rangle +(2e\hbar/mci)\,\langle 0\mid\hat{\imath}\times\nabla\mid 100\rangle]R^{-2}+O(R^{-3}), \tag{26}$$

where $\mathbf{\hat{1}}$ is the unit dyad; $\mathbf{r}_0$, the radius vector to the origin of the vector potential of the external magnetic field; and $\hat{\imath}$, a unit vector. With the exact wavefunction Musher[2] has shown that the second term of Eq. (26) cancels the first and hence there is no term in $\Delta\sigma$ proportional to R^{-2}. The proof of this statement makes use of the fact that

$$\mathbf{p}=(im/\hbar)[H,\mathbf{r}] \tag{27}$$

so that ψ_{0100} to order R^{-2} can be solved for immediately

[2] J. I. Musher, *Advances in Magnetic Resonance* (Academic Press Inc., New York, 1966), Vol. 2.

by, e.g.,

$$(\mathcal{H}_0-E_0)\,|\,0100\rangle=-\mathcal{H}_{0100}\,|\,0\rangle$$
$$=(e/2mc)\,(\mu_x/R^2)\,p_y\,|\,0\rangle$$
$$=(ie/\hbar c)\,(\mu_x/R^2)[H_0,\,y]\,|\,0\rangle \qquad (28)$$

so that

$$|\,0100\rangle=(ie/\hbar c)\,(\mu_x/R^2)\,y\,|\,0\rangle, \qquad (29)$$

where μ_x is the x component of $\boldsymbol{\mu}$.

The result that Hameka wished to explain by his calculation was that the intermolecular contribution to the effect of hydrogen bonding on σ in the NH_3 molecule depended on R^{-2} at large distances, as found by him in a previous calculation.[3] The reason for the apparence of this spurious term in the actual computation is that the commutation relationship, Eq. (27), only holds for exact wavefunctions or wavefunctions which are eigenfunctions of Hamiltonian containing no nonlocal potentials. As the NH_3 wavefunction which Hameka[3] used clearly does not satisfy these criteria (most wavefunctions and even the Hartree–Fock wavefunction are in this class) the above statement does not hold and $\Delta\sigma$ must contain spurious terms in R^{-2}. The reinterpretation of Hameka's result then implies that the "polarization" shift as suggested by Schneider *et al.*[4] rather than the "intermolecular" contribution should be dominant, at least at large distances.

III. MODEL (2)

A. Theory

In this section we obtain the chemical shift of the nucleus of a hydrogenic atom of nuclear charge ζe perturbed by a positive charge Ze located at a distance R. There are two cases: (i) R is parallel to H and (ii) R is perpendicular to H giving $\Delta_{||}$ and $\Delta\sigma_\perp$, respectively.

The chemical shift can be written in terms of the field induced at the nucleus as

$$\sigma=-\frac{H_{\text{ind}}}{H}=H^{-1}\int\frac{\hat{\imath}\times\mathbf{r}}{cr^3}\,d\tau, \qquad (30)$$

where $\hat{\imath}$ is the current induced by the external magnetic field of Hamiltonian

$$\mathcal{H}_{10}=-(e\hbar/2mci)\mathbf{H}\cdot\mathbf{r}\times\boldsymbol{\nabla} \qquad (31)$$

and by the electric field of the point charge of Hamiltonian

$$\mathcal{H}_{01}=-Ze^2\sum(r^n/R^{n+1})\,P_n(\cos\theta) \qquad (32)$$

when expanded about R, which is assumed to be located on the z axis. For R along the y axis $\mathcal{H}_{01}$ is obtained by a trivial rotation. The expression for the current density vector $\hat{\imath}$ is

$$\hat{\imath}=-(e^2/2mc)\,(\mathbf{H}\times\mathbf{r})\Psi^*\Psi+(e\hbar/2mi)\,\{\psi^*\nabla\psi-\psi\nabla\psi^*\}, \qquad (33)$$

where Ψ is the wavefunction only in the presence of $\mathcal{H}_{10}$ and $\mathcal{H}_{01}$ and is assumed normalized. The perturbation due to the magnetic moment enters only through the interaction of $\hat{\imath}$ and $\mathbf{A}_\mu$, Eq. (4), but in general one must be careful with this procedure to make sure that all the necessary terms have been included.

B. Calculation and Results

Again one expands Ψ in a double perturbation series as

$$\Psi=\psi_0+\mu\psi_{01}+\lambda\mu\psi_{11}+\mu^2\psi_{02} \qquad (34)$$

with ψ_0 given by Eq. (17). Dalgarno and Stewart[5] have given ψ_{01} and ψ_{02} as

$$\psi_{01}=\frac{Z}{\zeta}\psi_0\sum_{n=1}^{\infty}\frac{{a_0}^{n+1}}{R^{n+1}}\left[\frac{r^{n+1}}{(n+1)\,{a_0}^{n+1}}+\frac{r^n}{\zeta n{a_0}^n}\right]P_n(\cos\theta), \qquad (35)$$

$$\psi_{02}=(Z^2/\zeta^2)\psi_0\sum_n\sum_l a_n{}^l(r)\,(a_0/R)^l P_n(\cos\theta), \qquad (36)$$

where a_0 is the Bohr radius and the functions $a_n{}^l(r)$ are in Ref. 5. To terms of order R^{-6}, ψ_{11} is

$$\psi_{11}=\omega He^{-r}\{(1/12\rho^2)\,(2r^3+11r^2+22r)\,P_1{}^1\sin\phi$$
$$+(1/24\rho^3)\,(r^4+\tfrac{13}{3}r^3+\tfrac{13}{2}r^2)\,P_2{}^2\sin2\phi+(1/80\rho^4)$$
$$\times(r^5+\tfrac{47}{12}r^4+\tfrac{47}{9}r^3)\,(\tfrac{1}{2}P_3{}^3\sin3\phi-P_3{}^1\sin\phi)$$
$$+(1/360\rho^5)\,(r^6+\tfrac{37}{10}r^5+\tfrac{37}{8}r^4)\,(\tfrac{1}{4}P_4{}^4\sin4\phi-P_4{}^2\sin2\phi)$$
$$-(1/8\rho^6)[(r^7/42)+\tfrac{633}{590}r^6+\tfrac{1897}{1475}r^5]P_5{}^1\sin\phi\} \qquad (37)$$

with

$$\omega=i(Z/\sqrt{\pi})\,(\zeta/a_0)^{3/2}(ea_0{}^2/2c\hbar)\zeta^{-3}, \qquad r=\zeta r',$$

where r' is in atomic units, $\rho=\zeta R/a_0$, and the $\cos\theta$ argument of the $P_l{}^m$'s is left out for brevity. We do not include terms in R^{-6} containing the angular functions $P_5{}^3\sin3\phi$ and $P_5{}^5\sin5\phi$ as these do not contribute to σ.

The total σ is often divided into two terms, which are quantitatively different for every choice of coordinate system for the vector potential in $\mathcal{H}_{10}$, as

$$\sigma^d=\frac{e^2}{2mc^2}\int\frac{\phi^*\phi}{r}\sin^2\theta\,d\tau, \qquad (38)$$

[3] H. F. Hameka, Nuovo Cimento **11**, 382 (1959).
[4] W. G. Schneider, H. J. Bernstein, and J. A. Pople, J. Chem. Phys. **28**, 601 (1958).
[5] A. Dalgarno and A. Stewart, Proc. Roy. Soc. (London) **A238**, 276 (1956).

where $\phi^*\phi$ is the electron density in the absence of the magnetic field and

$$\sigma^p = -\frac{e\hbar}{2mci}\int\left(\psi^*\frac{\partial\psi}{\partial\phi}-\psi\frac{\partial\psi^*}{\partial\phi}\right)\frac{1}{r^3}\,d\tau. \qquad (39)$$

We have assumed the coordinate system in $\mathcal{H}_{10}$ centered on the nucleus possessing the magnetic moment and that the magnetic field is in the z direction. In this example $\Delta\sigma^d$ and $\Delta\sigma^p$ correspond to $\Delta\sigma_1$ and $\Delta\sigma_2$, respectively, of Model 1. For the parallel case

$$\Delta\sigma_{||}{}^d=\Delta\sigma_{||}=\frac{e^2\zeta}{3mc^2a_0}\left[-\frac{7}{10}\frac{Z}{\zeta}\rho^{-3}-\frac{Z^2}{\zeta^2}\left(\frac{439}{40}\rho^{-4}+\frac{9071}{140}\rho^{-6}+\frac{439\,099}{672}\rho^{-8}\right)-\frac{257\,611}{1120}\frac{Z^3}{\zeta^3}\rho^{-7}-\frac{1\,020\,241}{4480}\frac{Z^4}{\zeta^4}\rho^{-8}\right]; \qquad (40)$$

since $\Delta\sigma_{||}{}^p$ vanishes by symmetry and for the perpendicular case we have

$$\Delta\sigma_\perp{}^d=\frac{e^2}{3mc^2}\frac{\zeta}{a_0}\left[\frac{7}{20}\frac{Z}{\zeta}\rho^{-3}-\frac{Z^2}{\zeta^2}\left(\frac{641}{80}\rho^{-4}+\frac{80\,717}{2240}\rho^{-6}+\frac{48\,781\,591}{107\,520}\rho^{-8}\right)-\frac{776\,033}{4480}\frac{Z^3}{\zeta^3}\rho^{-7}-\frac{9\,593\,291}{35\,840}\frac{Z^4}{\zeta^4}\rho^{-8}\right] \qquad (41)$$

and

$$\Delta\sigma_\perp{}^p=-\frac{e^2}{3mc^2}\frac{\zeta}{a_0}\left[\frac{Z^3}{\zeta^2}\left(\frac{233}{48}\rho^{-4}+\frac{2877}{80}\rho^{-6}+\frac{44\,217}{448}\rho^{-8}\right)+\frac{106\,207}{1920}\frac{Z^3}{\zeta^3}\rho^{-7}-\frac{7223}{96}\frac{Z^4}{\zeta^4}\rho^{-8}\right]. \qquad (42)$$

In Eqs. (40) to (42), $\rho=\zeta R/a_0$. The expressions Eqs. (40) to (42) are correct up to terms in Z^2/ζ^2. Since ψ, Eq. (34), does not contain ψ_{12} these expressions do not contain all the Z^3/ζ^3 and Z^4/ζ^4 terms. For small enough Z/ζ they should suffice.

The average value of $\Delta\sigma$, if the vector $\mathbf{R}$ is rotated relative to $\mathbf{H}$, as occurs for ionic molecules in liquids, is

$$\langle\Delta\sigma\rangle_{Av}=\frac{e^2}{3mc^2}\frac{\zeta}{a_0}\left[-\frac{Z^2}{\zeta^2}\left(\frac{881}{72}\rho^{-4}+\frac{77\,947}{1120}\rho^{-6}+\frac{10\,502\,399}{17\,920}\rho^{-8}\right)-\frac{329\,801}{1440}\frac{Z^3}{\zeta^3}\rho^{-7}-\frac{4\,704\,715}{23\,040}\frac{Z^4}{\zeta^4}\rho^{-8}\right]. \qquad (43)$$

As expected the terms in R^{-4} exactly correspond to the quadratic field effect first calculated by Marshall and Pople.[6] In $\Delta\sigma_{||}$ and $\Delta\sigma_\perp$ there are terms in R^{-3} arising from the interaction of the charge distribution with the field gradient. These terms were calculated by Buckingham and Lawley.[7] They cancel out in rotating systems but may be important in ion-doped molecular crystals. Concerning the Z^2/ζ^2 dependence of $\langle\Delta\sigma\rangle_{Av}$, Eq. (43), we note that the ρ^{-4} term contributes about 75% of it, while the terms in ρ^{-6} and ρ^{-8} give about 25% for ρ around 4 or 5 a.u. ($\rho=\zeta R/a_0$). These terms are not entirely negligible.

IV. CONCLUSIONS

We have considered two models simple enough to allow fairly complete solutions for their chemical shielding constants. In the first model we have obtained the shielding constant due to a hydrogen atom in a uniform electric field for a nucleus located at a large distance from the H atom. We see that the linear effect of the electric field on the shielding constant contains only exponentially decreasing terms and does not contain any R^{-2} dependence.[1] An immediate use of this model has to indicate that the R^{-2} dependence predicted[3] for the "intermolecular" contribution to the effect of hydrogen bonding on the proton shielding constant on the ammonia molecule is an artifact of the approximate calculation. These results can also be useful in estimating the contribution of "asymmetric" atoms and lone-pair electrons to the shielding constants of distant nuclei.

We next obtained the shielding constant of a hydrogenic atom perturbed by a positive charge Ze at a distance R. This shielding constant is expressed in a series in R^{-1}. With terms up to R^{-8} and Z^2 the term in R^{-4} (corresponding to the quadratic field effect) is about 70% of the total. The model can be useful in the interpretation of shielding constants for ion-doped molecular crystals.

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[6] T. W. Marshall and J. A. Pople, Mol. Phys. **1**, 199 (1958).
[7] A. D. Buckingham and K. P. Lawley, Mol. Phys. **3**, 219 (1960).